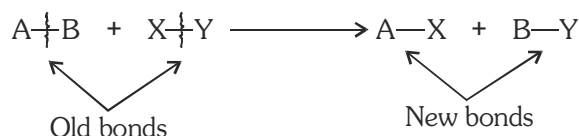


REACTION MECHANISM : PART-I

- ❑ **Reaction :** Breaking of old bond and formation of new bond is known as chemical reaction



A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. Reactants are of two types substrate and reagent.

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.

3.0 CONCEPTS TO UNDERSTAND REACTION MECHANISM :

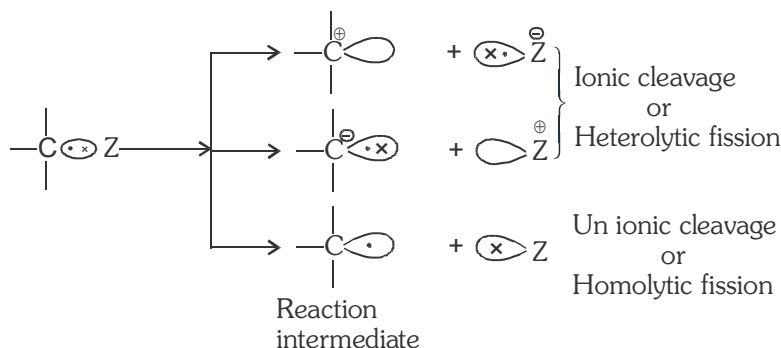
- (1) Bond cleavage (2) Attacking reagent (3) Reaction intermediate (4) Electronic effect

3.1 TYPE OF BOND CLEAVAGE :

(a) Heterolytical cleavage/fission : Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytical cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytical cleavage.

(b) Homolytical cleavage/fission : Cleavage in which equal distribution of e^- s takes place during the chemical reaction, is known as homolytical cleavage.

Due to equal distribution of electrons, without charge unpaired electron containing species are formed, which are known as free radicals and cleavage is known as unionic cleavage/homolytical fission.



3.2 TYPES OF ATTACKING REAGENTS

These are of two types :

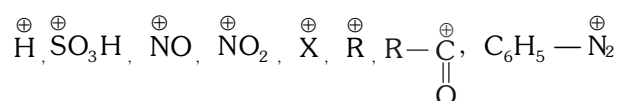
(a) Electrophilic reagent or electrophiles:

Electrophilic (electro + philic)
 (electron + loving)

The reagent which attacks on the negative part of the molecule or having attraction for electrons are called electrophiles.

Electrophiles may be positively charged or neutral.

(i) Positively charged electrophiles :



(ii) Neutral electrophiles :- central atom e^- deficient

(a) All Lewis acids as :

$\text{BF}_3, \text{AlCl}_3, \text{SO}_3, \text{ZnCl}_2, \text{BeCl}_2, \text{FeCl}_3, \text{SnCl}_2, \text{CO}_2, \text{SnCl}_4.$

(b) Free radicals, carbenes and nitrenes act as electrophiles.



(b) Nucleophilic reagent or nucleophiles

Which attacks on the positive site of the substrate or loves nucleus or having attraction towards nucleus.

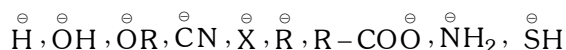
Nucleophilic (Nucleo + philes)



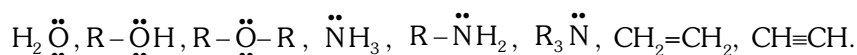
(Nucleus + loving)

Nucleophiles may be negatively charged ions or possess a lone pair of electron or πe^- .

(i) Negatively charged nucleophiles.



(ii) All Lewis base which contains lone pairs or πe^-



(iii) $\text{R}^*-\text{Mg}-\text{X}$, LiAlH_4^* , NaBH_4^*

The star (*) indicates the atom which donates electrons to the substrate.

Ambident nucleophile :- Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear a lone pair of electrons.

Examples :- $\text{K}^+\text{O}^--\text{N}=\text{O}$, $\ddot{\text{N}}\text{H}_2-\ddot{\text{O}}\text{H}$, $\text{Na}^+\text{C}^-\equiv\text{N}$

3.3 REACTION INTERMEDIATE

□ Carbocation :

Cation in which positive charge is present on carbon atom is called carbocation.

- ◆ Due to electron deficiency it acts as an electrophile and always attack on electron richer site.
- ◆ It is incomplete octet species because it has six electron in outer most shell.
- ◆ All electrons are paired.

□ Carbanions : Anion in which negative charge is present on carbon atom is called carbanion.

- ◆ It has eight electron in outermost shell so it is complete octet species.
- ◆ It is an electron richer species because it has extra electron.
- ◆ Due to presence of non bonding electrons it acts as a nucleophile.

□ Free Radical :

- ◆ Electrically neutral species in which unpaired electron is present on carbon atom is known as carbon free radical.
- ◆ It has seven electron or odd electron in outermost shell of unpaired electron containing carbon.
- ◆ It is electron deficient species due to incomplete octet.

□ Carbenes ($\text{CH}_2:$) :

Carbenes are neutral carbon species in which the carbon atom is bonded to two monovalent atoms or groups and carries two nonbonded electrons.

- It behaves as an electrophile.
- It is neutral.
- $6 e^-$ in outermost shell.
- $4 e^-$ are bonded and two are nonbonded e^- .

□ Nitrenes ($-\ddot{\text{N}}:$)

Nitrenes are neutral nitrogen species in which the nitrogen is bonded to one monovalent atom or group and carries four non-bonded electrons.

- It is monovalent radical.
- It is neutral.
- $6 e^-$ in outermost shell.
- Two are bonded and four are nonbonded electrons.



BEGINNER'S BOX-1

1. Which of the following is ambident nucleophile :-
(1) NH_2OH (2) NCO^\ominus (3) NO_2^\ominus (4) All of these
2. $\text{CH}_3\text{CH}_2\text{-Cl}$ undergoes homolytic fission to produce :-
(1) $\text{CH}_3\dot{\text{C}}\text{H}_2$ and $\dot{\text{C}}\text{H}_2\text{Cl}$ (2) $\text{CH}_3\dot{\text{C}}\text{H}_2$ and Cl^\ominus
(3) $\text{CH}_3\overset{\oplus}{\text{C}}\text{H}_2$ and Cl^\ominus (4) $\text{CH}_3\overset{\ominus}{\text{C}}\text{H}_2$ and Cl^\oplus
3. Which of the following intermediate has complete octet :-
(1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

3.4 ELECTRONIC EFFECTS :

There are four effects which affect the chemical reaction due to transfer of electron

- (1) Inductive effect (2) Mesomeric effect
(3) Hyperconjugation (4) Electromeric effect

3.4.1 INDUCTIVE EFFECT (I-EFFECT) :

- ◆ Polarity induced in non polar σ bond due presence of adjacent polar bond is known as inductive effect.

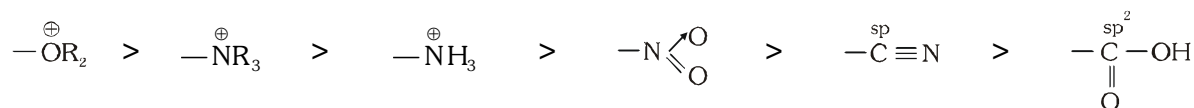
GOLDEN KEY POINTS

- In I-effect there is partial displacement of e^\ominus .
- After 3 or 4 C-atom I-effect is considered to be zero.
- Inductive effect decreases on increasing distance.

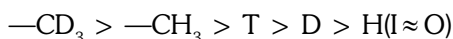
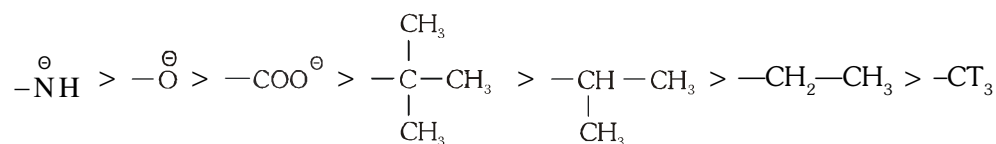
So **Magnitude of I effect** $\propto \frac{1}{\text{distance}}$

- I-effect of hydrogen is considered as zero.

-I groups :



+I groups :

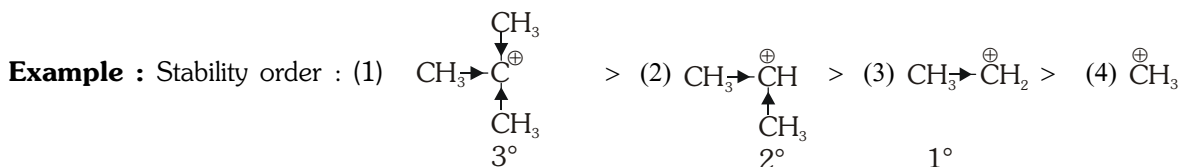


APPLICATION OF I-EFFECT

(1) Stability of carbocation :

$$\text{Energy} \propto \text{charge} \propto \frac{1}{\text{stability}}$$

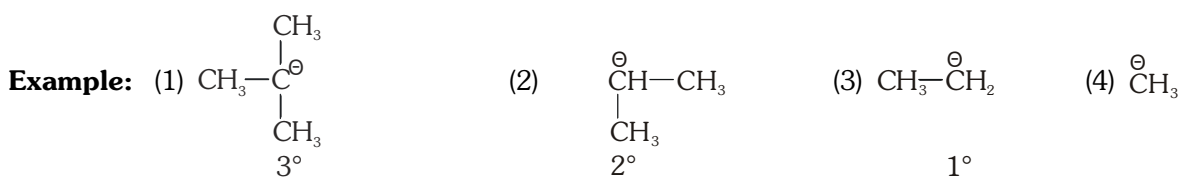
$$\text{Stability of carbocation} \propto \frac{+I \text{ effect}}{-I \text{ effect}}$$



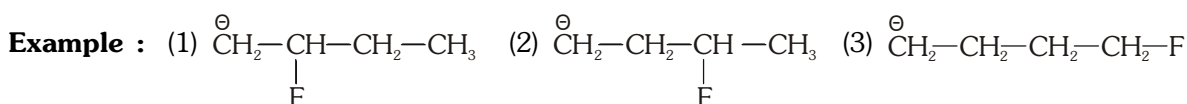
Reason : More no. of +I group.
more stable carbocation.
so stability order $1 > 2 > 3 > 4$.

(2) Stability of carbanion :

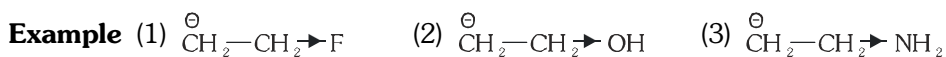
$$\text{Stability of Carbanion} \propto \frac{-I \text{ effect}}{+I \text{ effect}}$$



More No. of +I group.
Less stable carbanion.
So stability order $4 > 3 > 2 > 1$



Minimum distance of -F.
Maximum -I of -F.
Minimum negative charge.
Maximum stable.
So stability order $1 > 2 > 3$

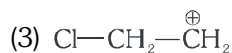
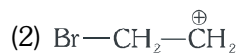


Maximum -I of F.
Negative charge will be minimum.
Maximum stable.
So stability order $1 > 2 > 3$

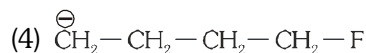
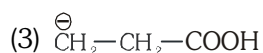
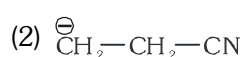
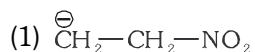


BEGINNER'S BOX-2

1. Most stable carbocation is :

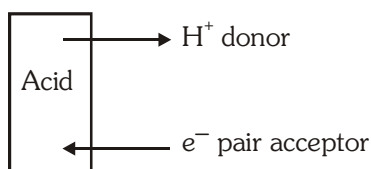


2. Most stable carbanion is :



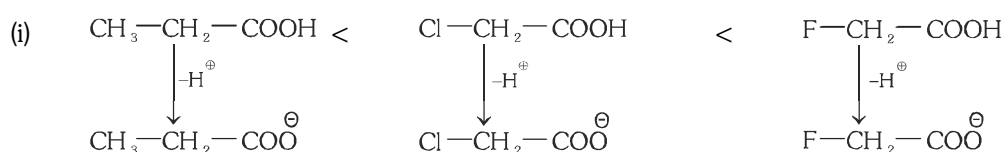
(3) Acidic and basic strength :

◆ **Acidic strength :**



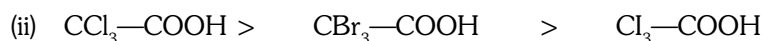
Acidic strength \propto Stability of conjugate base (anion) $\propto \frac{-\text{I effect}}{+\text{I effect}}$

Example :

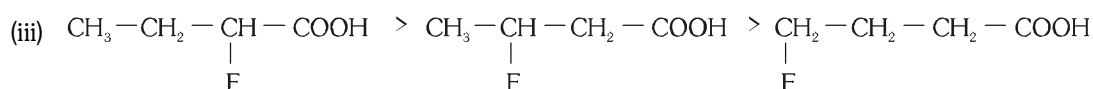


+I of $-\text{CH}_3$
anion is less stable

Maximum -I of $-\text{F}$
Maximum stable anion
Corresponding acid is maximum acidic.



maximum -I of Cl
so maximum acidic.

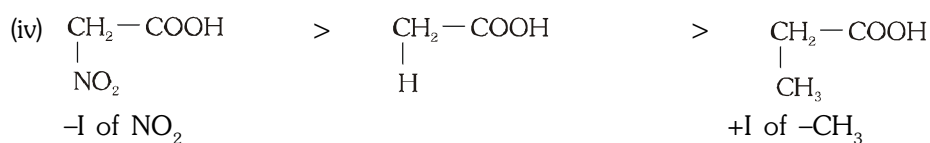


minimum distance of F from $-\text{COOH}$

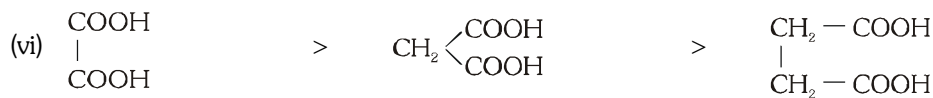
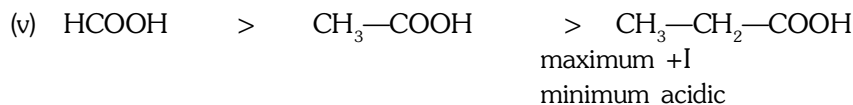
maximum -I of F.

So maximum acidic.





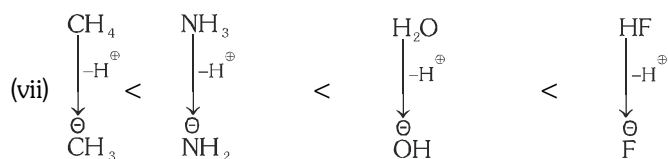
maximum acidic



minimum distance of $-\text{COOH}$ from other

maximum -I of $-\text{COOH}$ on other

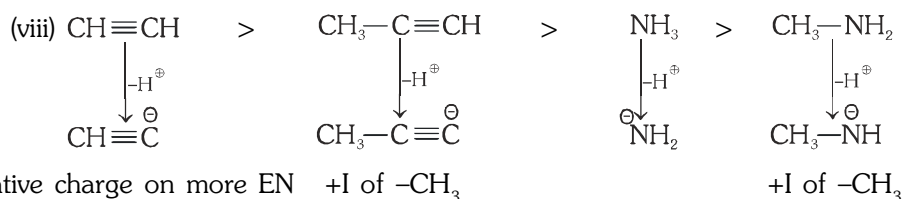
maximum acidic



Negative charge on maximum E.N.

Maximum stable anion

So corresponding acid is most acidic

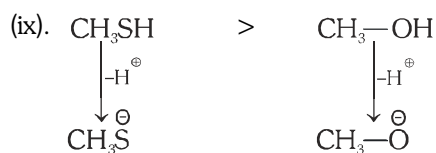


negative charge on more EN

atom and no +I

anion is maximum stable

so corresponding acid is most acidic

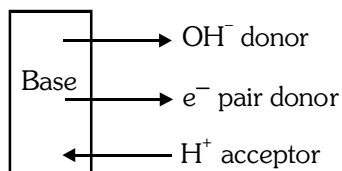


negative charge on big size atom

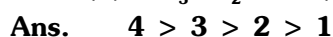
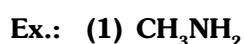
more stable anion

so corresponding acid is more acidic

◆ Basic strength :



$$\text{Basic strength} \propto +\text{I effect} \propto \frac{1}{-\text{I effect}}$$



Maximum +I

so maximum basic



BEGINNER'S BOX-3

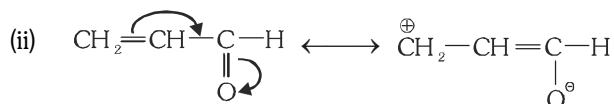
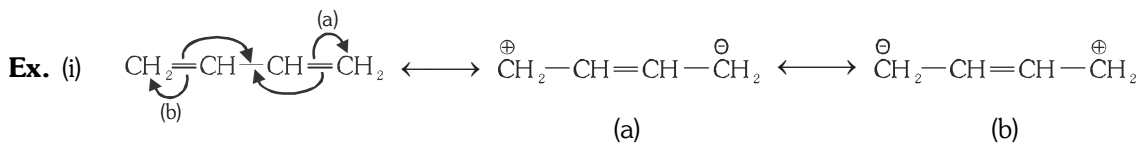
- Which of the following is most acidic :
 (1) $\text{Cl}_3\text{C}-\text{COOH}$ (2) $\text{Cl}_2\text{CH}-\text{COOH}$ (3) $\text{ClCH}_2-\text{COOH}$ (4) CH_3COOH
- Which of the following is most acidic :
 (1) $\begin{array}{c} \text{CH}_2-\text{COOH} \\ | \\ \text{F} \end{array}$ (2) $\begin{array}{c} \text{CH}_2-\text{COOH} \\ | \\ \text{Cl} \end{array}$
 (3) $\begin{array}{c} \text{CH}_2-\text{COOH} \\ | \\ \text{Br} \end{array}$ (4) $\begin{array}{c} \text{CH}_2-\text{COOH} \\ | \\ \text{I} \end{array}$
- Which is most basic among the following :
 (1) $\text{CH}_3\text{CH}_2-\text{NH}_2$ (2) $\text{Cl}-\text{CH}_2\text{CH}_2\text{NH}_2$
 (3) $\text{O}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}_2$ (4) ${}^-\text{O}-\text{CH}_2\text{CH}_2-\text{NH}_2$

3.4.2 RESONANCE OR MESOMERIC EFFECT

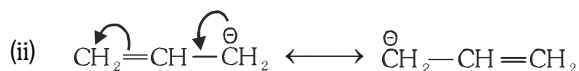
Delocalization of πe^- is called as resonance or complete transfer of πe^- from one shell to another shell is called as **Resonance**.

Conditions For Resonance

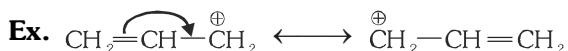
- (1) If there are two π bonds in conjugation then e^- of one π bond are transferred towards another π bond.



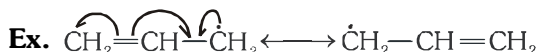
- (2) If there is lone pair or a negative charge and π bond are in conjugation then lone pair of e^- or negative charge are transferred towards π bond.



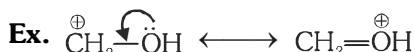
- (3) If there is positive charge (vacant orbital) and π bond are in conjugation then e^- of π bond are transferred towards positive charge.



- (4) If there is free e^- and π bond are in conjugation.



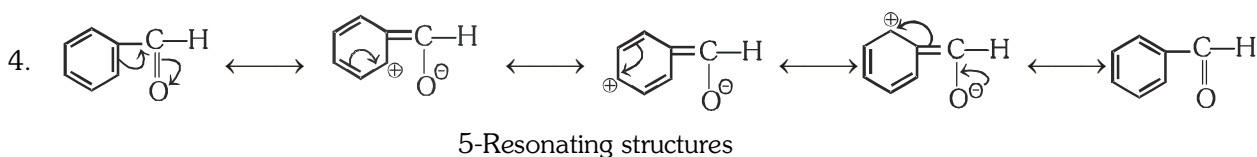
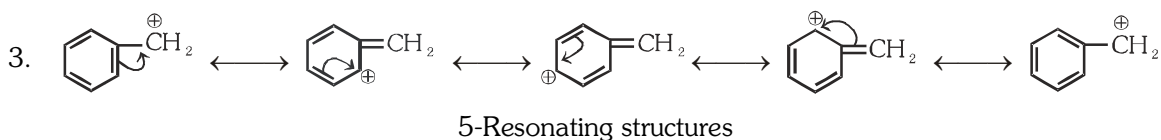
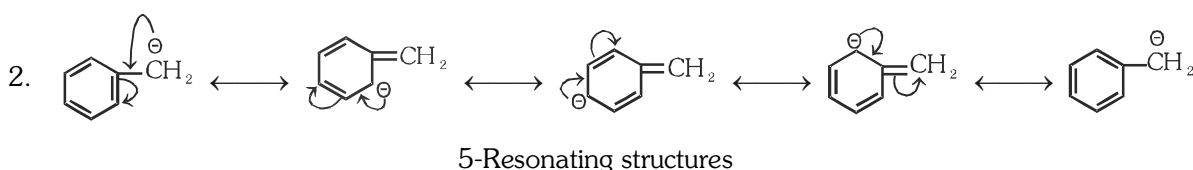
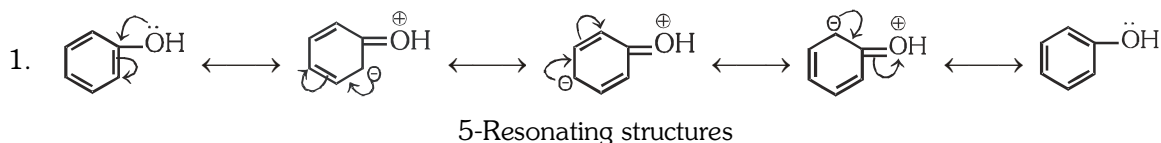
- (5) If there is lone pair or negative charge and positive charge (vacant orbital) are in conjugation then e^- of lone pair or negative charge are transferred towards positive charge.



GOLDEN KEY POINTS

- In resonance only e^- are delocalised not atoms.
- The number of e^- or number of unpaired or paired e^- in all resonating structures should be same.
- It is permanent effect.
- All the resonating or canonical structures must follow the Lewis structures.

Draw resonating structures :

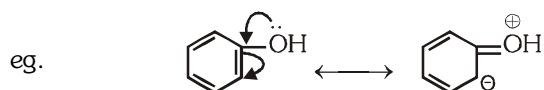


M-effect : Delocalisation of electron in conjugated system (due to presence of EWG or EDG) is known as 'M' effect.

(1) +M effect :- Group that donates the electron pair to conjugated system is known as +M effect exerting groups and the phenomena is known as +M effect.

+M group : Lone pair containing group like

e.g. $-\ddot{\text{N}}\text{H}_2$, $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$, $-\ddot{\text{N}}\text{R}_2$, $-\ddot{\text{S}}\text{H}$, $-\ddot{\text{N}}\text{HR}$, $-\ddot{\text{X}}$, $-\ddot{\text{N}}\text{HCOCH}_3$

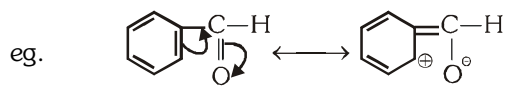


-OH group lone pair donor

So + M of -OH group

(2) -M effect :- Group, that withdraws electron pair from the conjugated system, is known as -M effect exerting groups and the phenomena is known as -M effect.

-M group : $-\text{CHO}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{COR}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{COX}$, $-\text{CONH}_2$, $-\text{SO}_3\text{H}$



-CHO group withdrawing e^- .

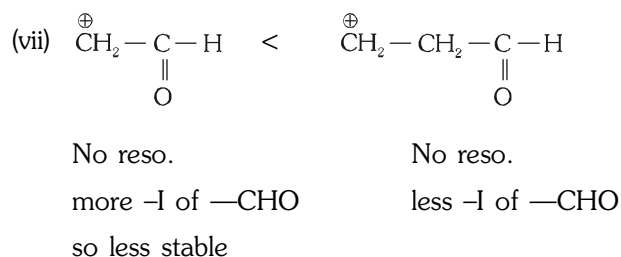
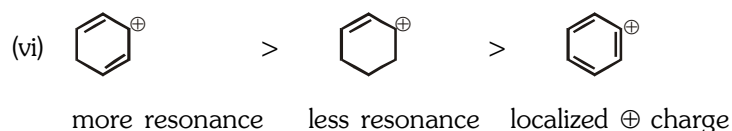
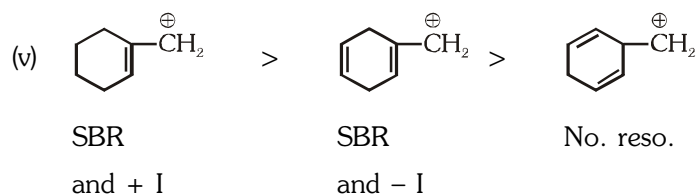
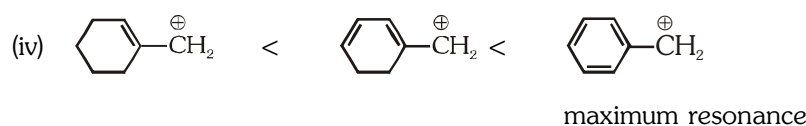
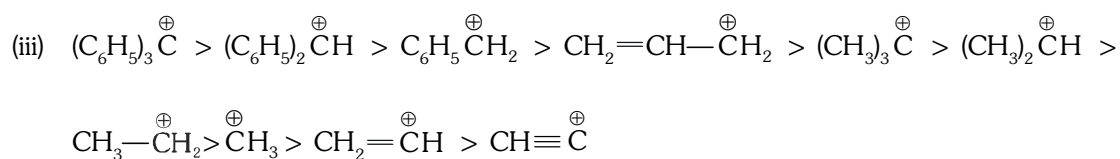
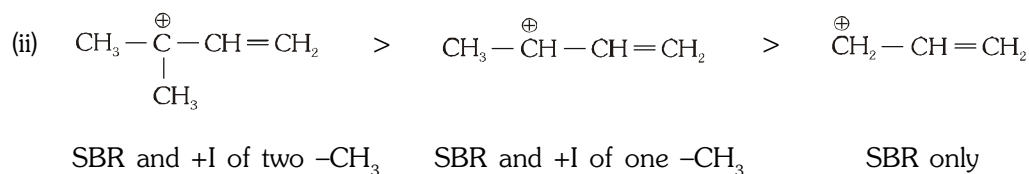
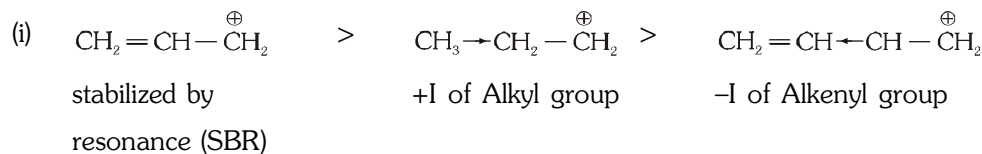
So -CHO is -M group



APPLICATIONS OF RESONANCE EFFECT :

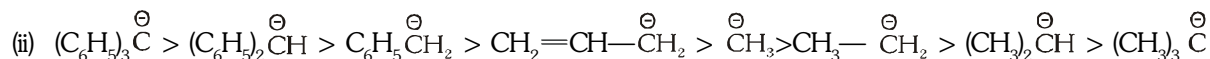
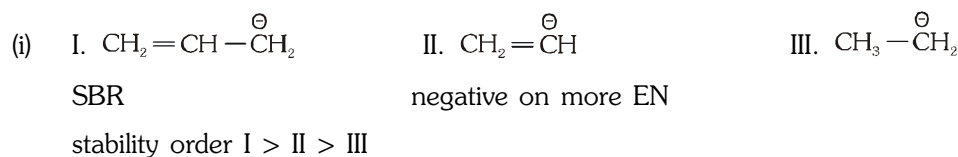
(1) Stability of carbocation.

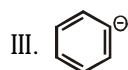
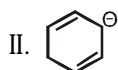
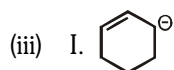
Ex. Give stability order for :-



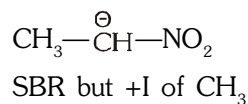
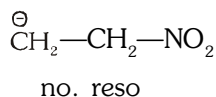
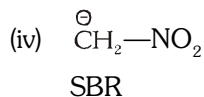
(2) Stability of carbanion :

Ex. Give stability order of :

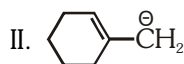
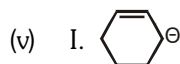




resonance stable more resonance stable localized \ominus charge
stability order $\text{II} > \text{I} > \text{III}$



stability order $\text{I} > \text{III} > \text{II}$



SBR and +I

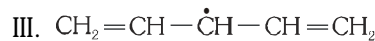
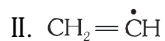
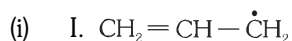
SBR

SBR and more +I

stability order $\text{II} > \text{I} > \text{III}$

(3) Stability of free radicals.

Ex. Give stability order for :

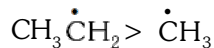
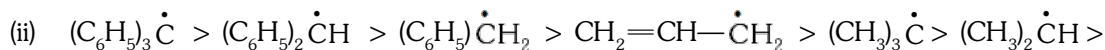


less resonance

no resonance

more resonance

stability order $\text{III} > \text{I} > \text{II}$



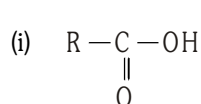
(4) Stability of resonating structures (R.S) Rules :

(i) Complete octet R.S. is more stable than incomplete octet.

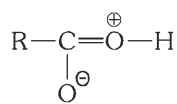
(ii) Nonpolar R.S. is more stable than polar resonating structures.

(iii) For charged R.S. negative charge on more EN and positive charge on less EN is more stable.

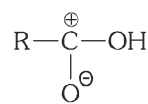
Ex. Arrange the following for stability order.



>



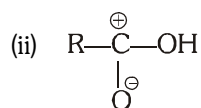
>



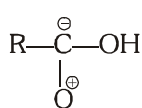
complete octet, nonpolar

complete octet, polar

incomplete octet



>



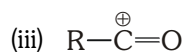
less EN atom

more EN atom with

with incomplete octet

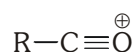
incomplete octet



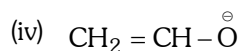


incomplete octet

<

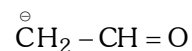


complete octet



(negative charge on more EN)

>











(negative charge on less EN)

(5) Aromaticity (Huckel's rule) : Cyclic, planar and completely conjugated system with $(4n+2)\pi$ electrons (where $n = 0, 1, 2, 3, \dots$) is known as aromatic compounds, these compound gains extra stability which is known as aromaticity.

Note : $[4n + 2]$ π electrons. (Odd number of π electron pairs) means

If $n = 0$	2π electrons	or 1 pair
$n = 1$	6π electrons	or 3 pairs
$n = 2$	10π electrons	or 5 pairs
$n = 3$	14π electrons	or 7 pairs

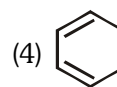
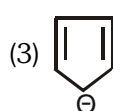
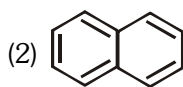
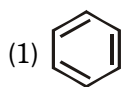
S.No	Compound	Cyclic	Planar	Cyclic Resonance	Huckel Rule $(4n+2) \pi e^-$	Aromatic Yes/No
1.		✓	✓	✓	$2\pi e^-$	Yes
2.		✓	✓	✓	$4\pi e^-$	No
3.		✓	✓	✓	$4\pi e^-$	No
4.		✓	✓	✓	$6\pi e^-$	Yes
5.		✓	✓	✓	$6\pi e^-$	Yes
6.		✓	✗	✗	$4\pi e^-$	No
7.		✓	✓	✓	$6\pi e^-$	Yes
8.		✓	✓	✓	$6\pi e^-$	Yes



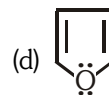
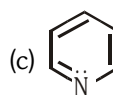
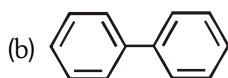
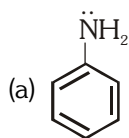
9.		✓	✓	✓	$6\pi e^-$	Yes
10.		✓	✓	✓	$6\pi e^-$	Yes
11.		✓	✓	✓	$6\pi e^-$	Yes
12.		✓	✓	✓	$10\pi e^-$	Yes
13.		✓	✓	✓	$14\pi e^-$	Yes
14.		✓	✓	✓	$6\pi e^-$	Yes
15.		✓	✗	✗	$6\pi e^-$	No
16.		✓	✓	✓	$6\pi e^- + 6\pi e^-$	Yes

BEGINNER'S BOX-4

1. Which of the following is nonaromatic



2. Which of the following compounds are aromatic in nature



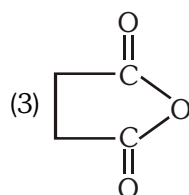
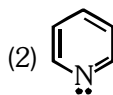
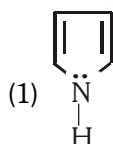
(1) Only a

(2) a and b

(3) a,b,d

(4) all of these

3. Which of the following is not aromatic compound



(4) All of these



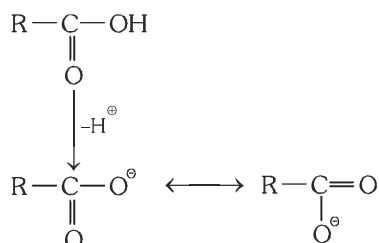
(6) Acidic and Basic strength :

(a) **Acidic strength :** $\left(\text{Acidic strength} \propto \text{stability of conjugate base (anion)} \propto \frac{-M, -I}{+M + I} \right)$

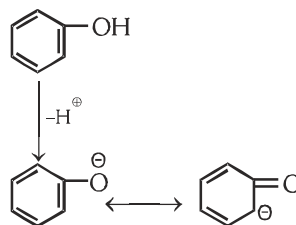
Illustrations

Illustration 1. Carboxylic acids are more acidic than phenols, why ?

Solution.



2, equal R.S. more stable anion
so corresponding acid is more acidic.
Here, carboxylate ion is more stable
than phenoxide ion.

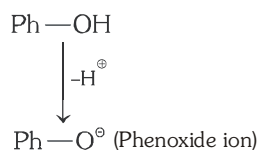


5, unequal R.S. less stable anion since -ve
charge is being shared by oxygen is less
electronegative carbon.

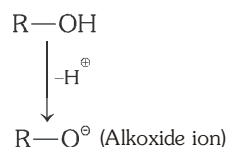
Note : The molecule having equivalent R.S. has more stability than the molecule having non equivalent R.S.

Illustration 2. Phenol is more acidic than alcohols why ?

Solution.



anion stable by resonance
So, corresponding acid is more acidic.



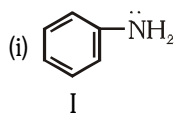
no resonance.
less stable anion

(b) Basic strength order :- Tendency to donate the electron pair by an atom or group is known as its basic strength. Compounds in which electron pair is delocalised will be less basic while, Those in which electron pair is localised will be more basic.

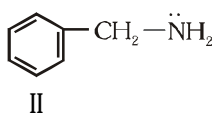
$$\left(\text{Basic strength} \propto \text{H}^{\oplus} \text{ accepting tendency} \propto \text{l.p. donating tendency} \propto \frac{+M, +I}{-M - I} \right)$$

Ex.

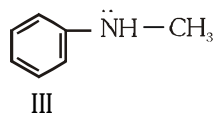
Give basic strength order :



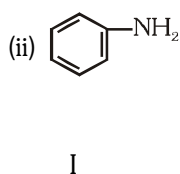
l.p. is stabilized by
resonance
basic order —



no reso. of l.p.
so maximum basic
III > I



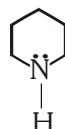
l.p. is stabilized by resonance
and +I of CH₃



SBR
basic order —

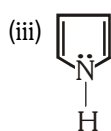


localized l.p.
on more EN
III > II > I



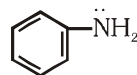
localized l.p.
on less EN



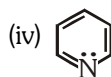


more resonance of l.p.
so less basic

<



less resonance of l.p.
so more basic



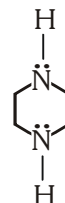
I
l.p. on
more EN
so minimum basic
So, basic order



II
more -I
of oxygen



III
+I

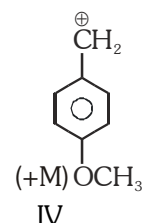
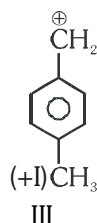
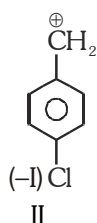
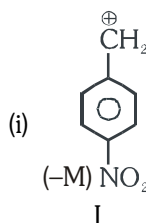


IV
less -I of
nitrogen

III > IV > II > I

Illustrations

Illustration 3. Give stability order of :

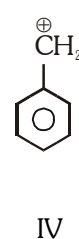
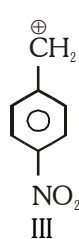
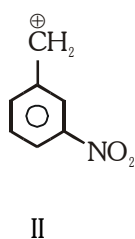
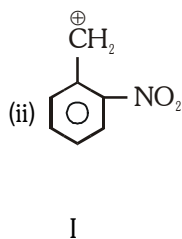


charge ↑
So stability order

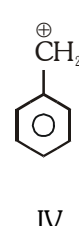
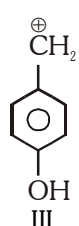
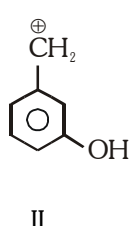
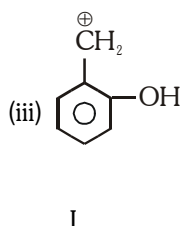
charge ↑
IV > III > II > I

charge ↓

charge ↓



$-M_o = -M_p$ and $-M_m = 0$
but $-I_o > -I_m > -I_p$, $-M$ and $-I$ increases positive charge.
stability order is IV > II > III > I



$-OH$ group shows $+M$ effect
 $+M_o = +M_p$ and $+M_m = 0$ but $-I_o > -I_m > -I_p$ and $+M \gg -I$
So $+M$ stabilize the carbocation by decreasing positive charge
Stability order III > I > IV > II



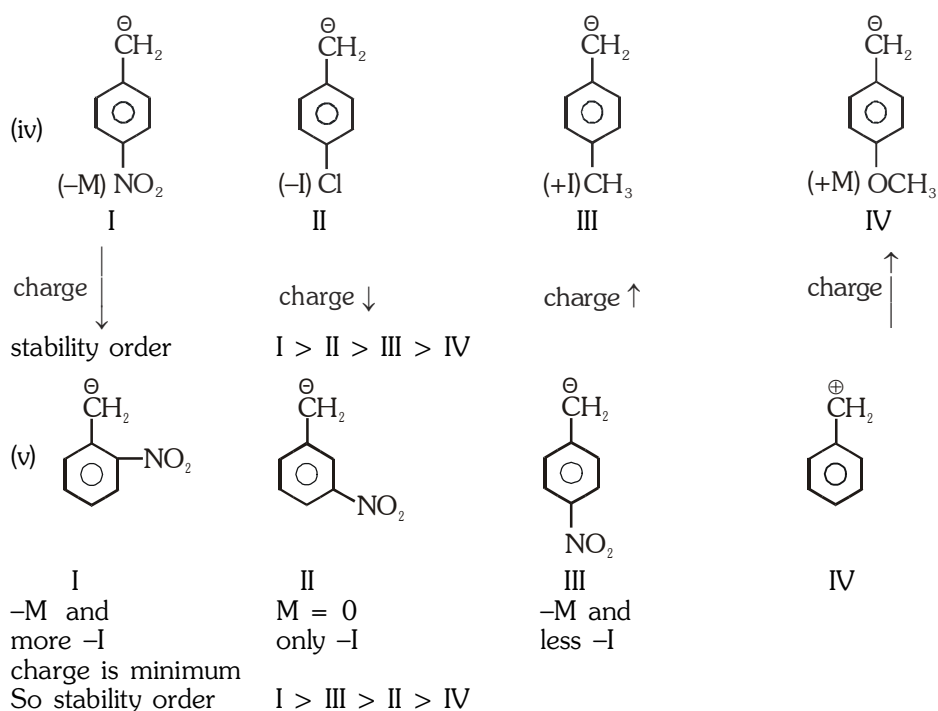
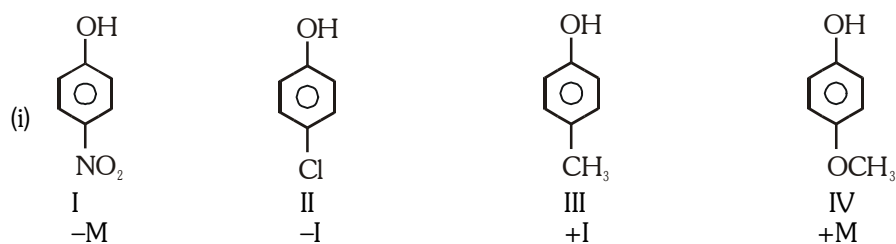
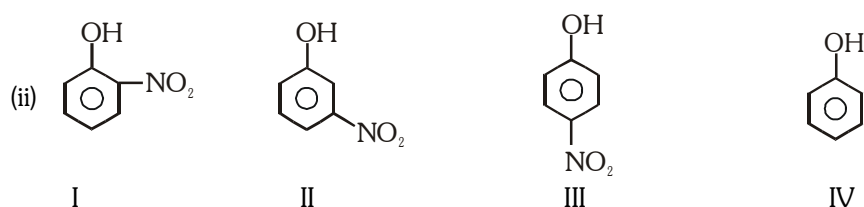


Illustration 4. Give acidic strength order for :



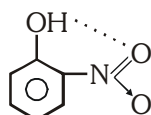
So acidic order is I > II > III > IV



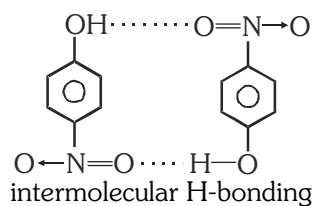
-M and more -I M = 0 only -I -M and less -I

Acidic order should be I > III > II > IV but correct order is III > I > II > IV

Reason : Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.



- intramolecular H-bonding
- less association
- less B.P.
- more volatile
- less acidic
- less soluble in water.



intermolecular H-bonding

more association

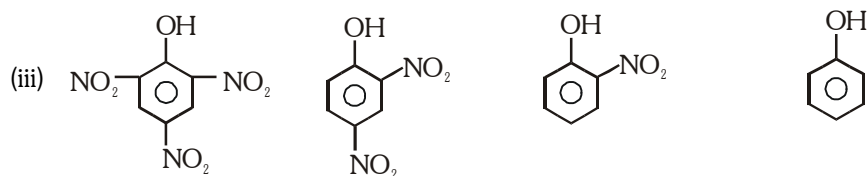
more B.P.

less volatile

more acidic

more soluble in water.





I

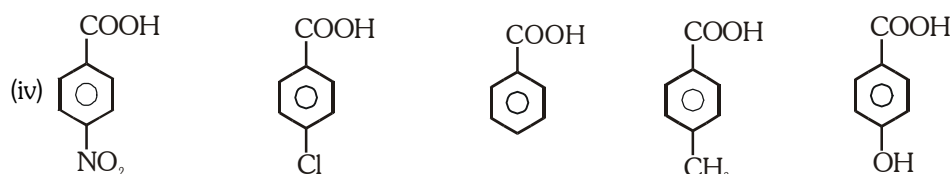
II

III

IV

maximum -M and
maximum -I effect
so maximum acidic

Acidic order $I > II > III > IV$



I

II

III

IV

V

-M

-I

+I

+M

acidic order is $I > II > III > IV > V$

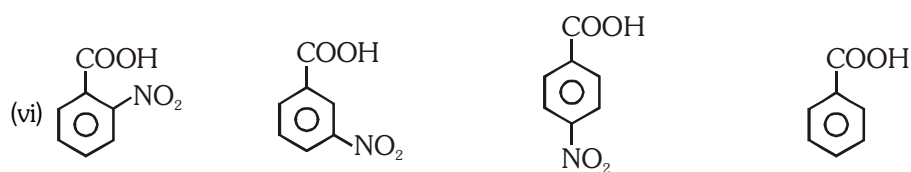


I

II

III

Acidic order is $I > III > II$

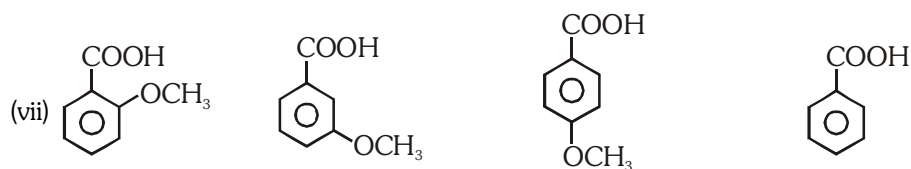


ortho effect

only -I

-I and -M

Acidic order is $\Rightarrow o > p > m > \text{benzoic acid}$

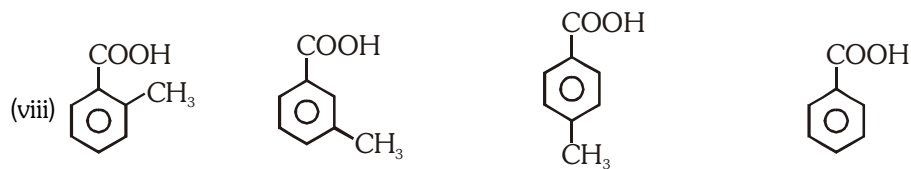


ortho effect

only -I

-I and +M

Acidic order is $\Rightarrow o > m > \text{benzoic acid} > p$

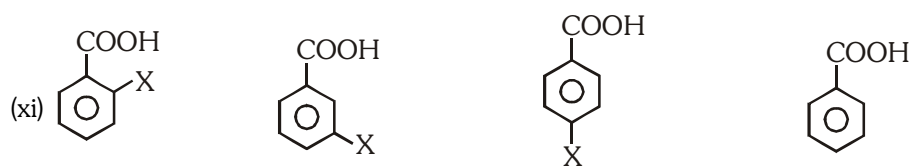


ortho effect

only +I

+I and +H

Acidic order is $\Rightarrow o > \text{benzoic acid} > m > p$



ortho effect

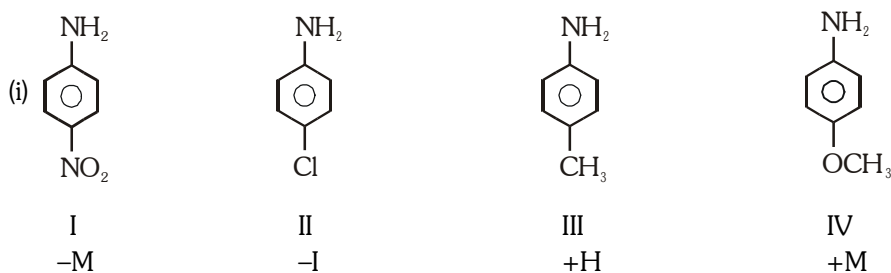
-I (more)

-I (less)

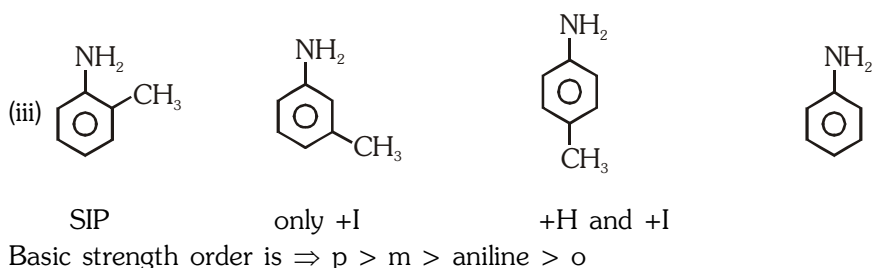
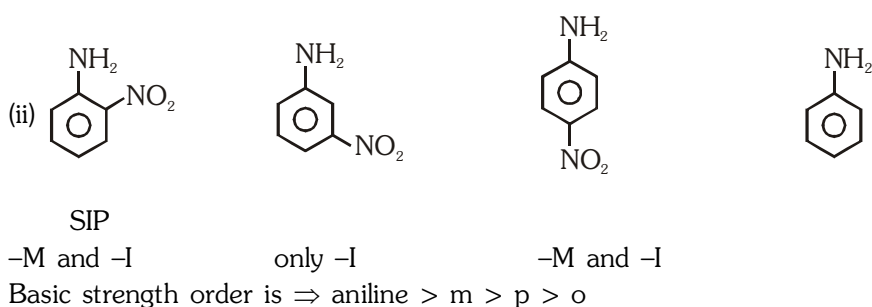
Acidic order is $\Rightarrow o > m > p > \text{benzoic acid}$



Illustration 5. Give basic strength order for :



Basic strength order $IV > III > II > I$

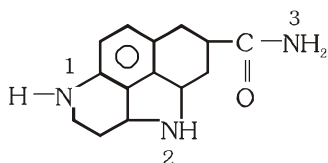


BEGINNER'S BOX-5

1. Most acidic among the following is :



2. Which nitrogen is most basic :-



- | | | | |
|-------|-------|-------|---------------------------|
| (1) 1 | (2) 2 | (3) 3 | (4) All are equally basic |
|-------|-------|-------|---------------------------|

3. Which is strongest base ?



4. Which is weakest base :

- | | |
|------------------------|---------------------------|
| (1) $C_6H_5-CH_2-NH_2$ | (2) $C_6H_5-CH_2-NH-CH_3$ |
| (3) $O_2N-CH_2-NH_2$ | (4) $CH_3-NH-CHO$ |



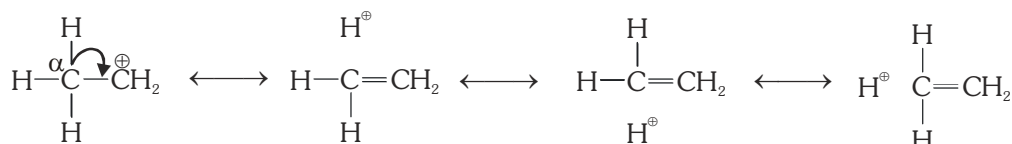
3.4.3 HYPERCONJUGATION EFFECT (H-EFFECT)

Complete transfer of e^- of C-H σ bond towards π bond or positive charge or free electron is called as H-effect (permanent effect). It is also called as No bond resonance (given by Nathen and Baker).

□ CONDITIONS OF H-EFFECT :

1. If there is C-H σ bond and positive charge are in conjugation

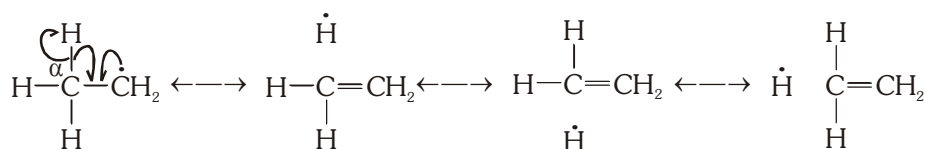
Carbon which is attached to positively charged carbon is called as α -C and H which is attached to α -C is called as α -H. So if number of α -H are more, then there will be more number of hyperconjugating structures, so more stable will be the carbocation.



all are called as hyperconjugating structures or canonical structures.

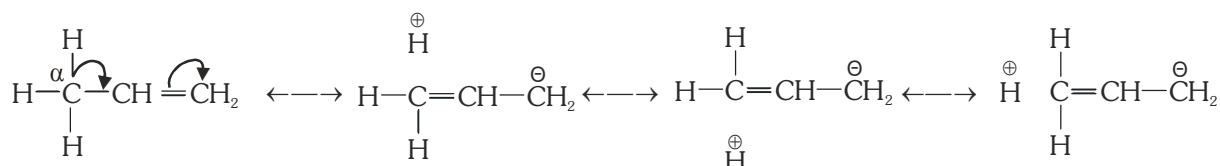
2. If there is C-H σ bond and free e^- are in conjugation then there will be H-effect.

Carbon, which is attached to C having unpaired e^- , is called as α -C and H which are attached to α -C are called as α -H.

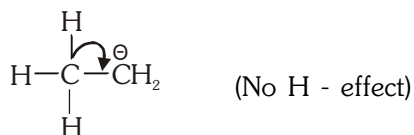


3. If there is C-H σ bond and π bond are in conjugation then there will be H-effect.

sp^3 carbon which is attached to double bonded C is called as α -C and H attached to α -C is called as α -H.



Note : If there is C-H σ bond and negative charge in conjugation then there will be no H-effect.



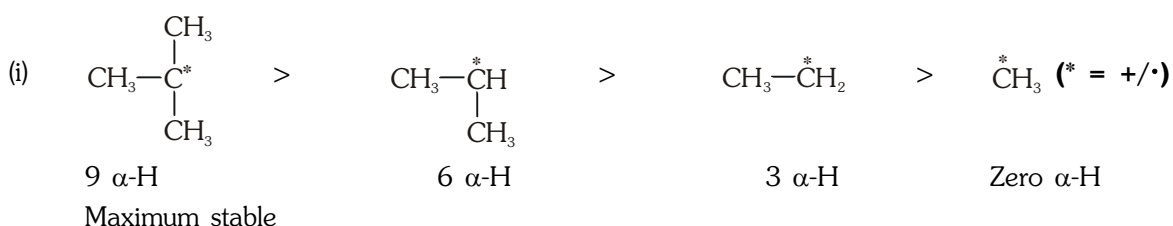
no shifting of C-H σ bond, because anion is having complete octet. ($8e^-$)

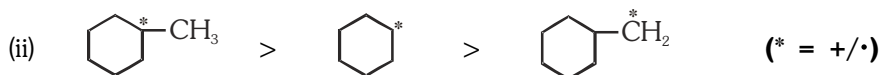
□ APPLICATION OF H-EFFECT

□ Stability of carbocation / Free Radical /Alkene

◆ Stability \propto No. of canonical structures \propto No. of α H.

Example : Give stability order for :-



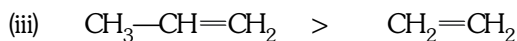


7 α -H

4 α -H

1 α -H

Maximum stable

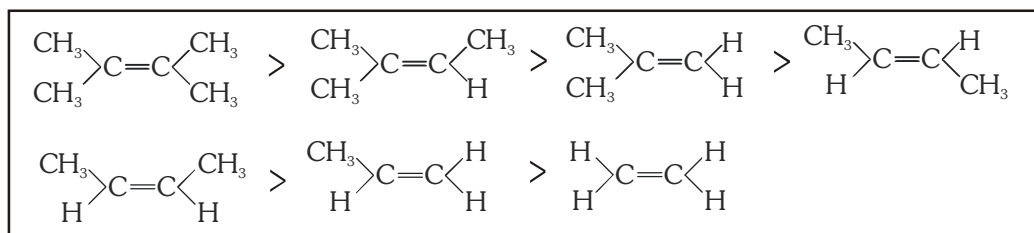


3 α -H

Zero α -H

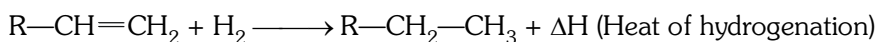
more stable

(iv) Stability order of alkenes will be



GOLDEN KEY POINTS

Heat of hydrogenation :



Heat evolved when any unsaturated hydrocarbon is hydrogenated is called heat of hydrogenation (ΔH)

(If alkene is more reactive towards hydrogen then it will evolve more ΔH)

So,
$$\text{Heat of hydrogenation} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{number of } \alpha\text{-H}}$$

BEGINNER'S BOX-6

1. Which of the following alkene is most stable ($\text{R} = \text{CH}_3$).

- (1) $\text{R}_2\text{C=CR}_2$ (2) R—CH=CR_2 (3) R—CH=CH—R (4) R—CH=CH_2

Which of the following has minimum heat of hydrogenation.

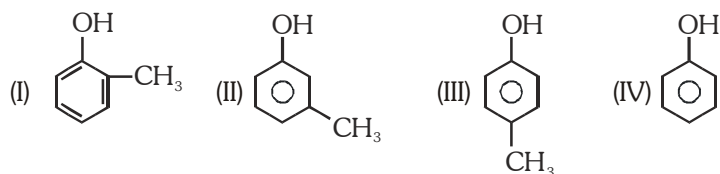
- (1) ethene (2) Propene (3) cis-2-butene (4) trans-2-butene

3. Which of the following is most stable.

- (1) Conjugated alkadiene ($\text{CH}_2\text{=CH—CH=CH}_2$)
 (2) Isolated alkadiene ($\text{CH}_2\text{=CH—CH}_2\text{—CH=CH}_2$)
 (3) Cumulated alkadiene ($\text{CH}_2\text{=C=CH}_2$)
 (4) All are equal.



4. What is the order of acidic strength of given molecules



(1) I > II > III > IV

(2) IV > III > II > I

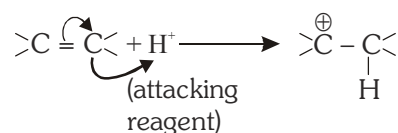
(3) IV > II > III > I

(4) I > II > IV > III

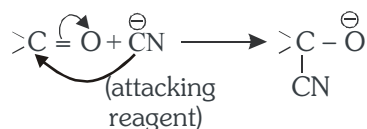
3.4.4 ELECTROMERIC EFFECT : (E Effect)

Complete transfer of a shared pair of π -electrons from one atom to another atom in presence of attacking reagent, is known as 'E' effect.

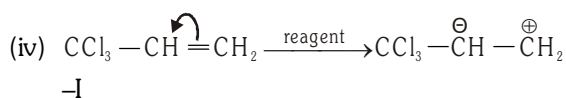
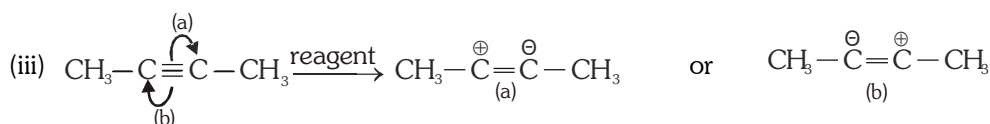
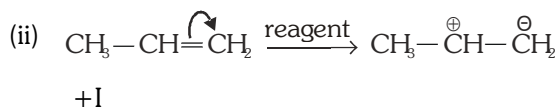
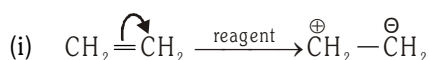
- (i) **Positive Electromeric Effect (+ E effect)** : In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



- (ii) **Negative Electromeric Effect (-E effect)** : In this effect the π -electrons of the multiple bond are transferred to that atom, to which the attacking reagent does not get attached. For example.

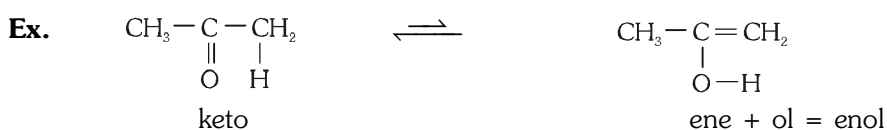
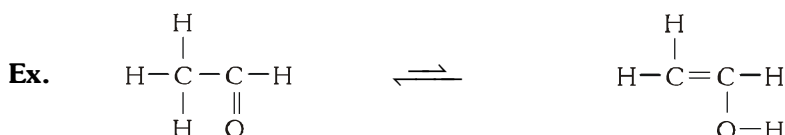
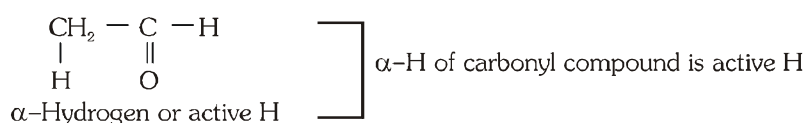


Shifting of π electrons :



3.5 TAUTOMERISM OR DESMOTROPISM

- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen from one polyvalent atom to another polyvalent atom. This phenomena is known as tautomerism.
- Desmotropism means bond turning. [Desmos = Bond ; Tropos = Turn]

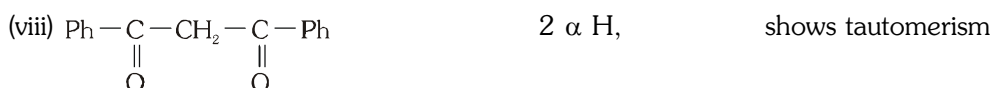
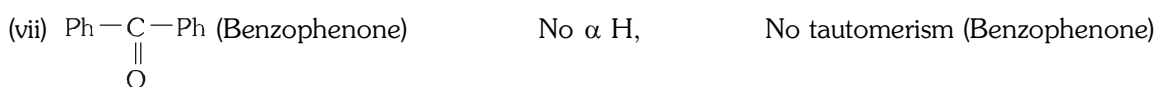
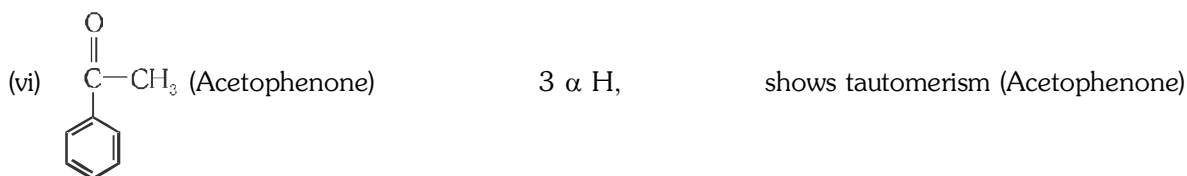
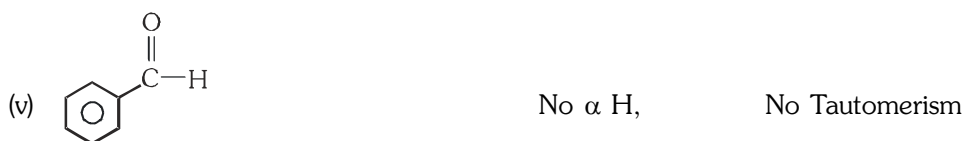


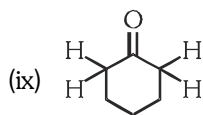
Note : (1) Tautomers exist in dynamic equilibrium.

(2) By shifting of H-atom, π bond also changes its position.

(I) Condition for Tautomerism :

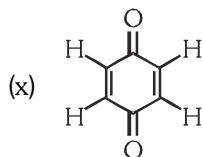
(a) For carbonyl compounds :- Carbonyl compounds having at least one active-H (α -H) show tautomerism





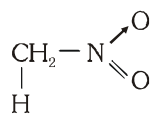
4 α H,

shows tautomerism

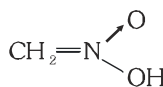


α -H, attached sp^2 carbon does not initiate in tautomerism

(b) For nitro compounds : Nitro compounds having at least one active-H (α - H) show tautomerism



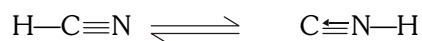
Nitro form



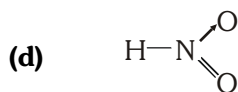
Acinitro form

(acidic form so soluble in base)

(c) $H-C\equiv N$ and $H-N\equiv C$ are tautomers [also Functional isomers] while $R-C\equiv N$ and $R-N\equiv C$ are only Functional isomers.



Active H

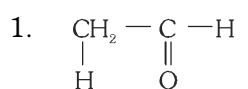


and

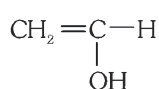
$H-O-N=O$ are tautomers.

Note : Nitro compounds with at least one α -H are soluble in NaOH.

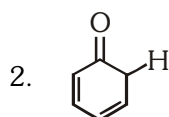
(II) Enol Content :



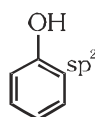
"keto" ($\approx 99\%$)



"enol" ($\approx 1\%$)



"keto" ($\approx 1\%$)



"enol" (stable by resonance and aromatic nature) ($\approx 99\%$)

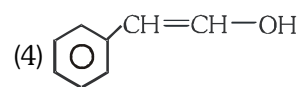
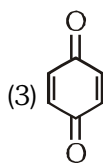
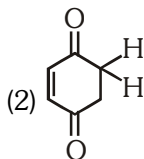
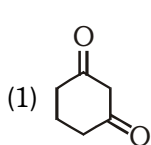
GOLDEN KEY POINTS

- More active the H, more will be its participation in tautomerism.
- Stability of enol form depends on (i) Resonance and (ii) H - Bond (iii) Aromaticity.

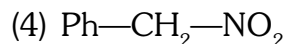
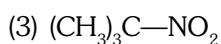
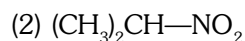
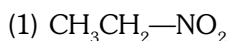


BEGINNER'S BOX-7

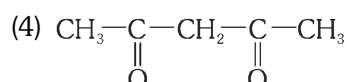
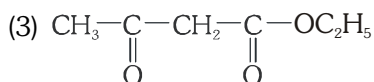
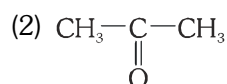
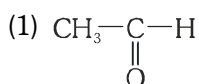
1. Which of the following does not show keto enol tautomerism.



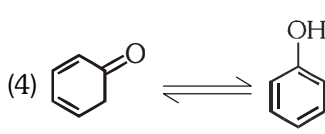
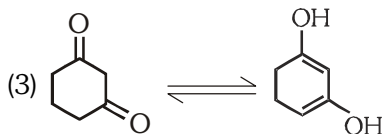
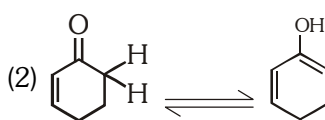
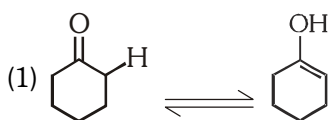
2. Which of the following is not soluble in NaOH.



3. Which of the following has highest enol content.



4. In which of the following reaction most stable enol is present.



ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	
	Ans.	4	1	2	
BEGINNER'S BOX-2	Que.	1	2		
	Ans.	1	1		
BEGINNER'S BOX-3	Que.	1	2	3	
	Ans.	1	1	4	
BEGINNER'S BOX-4	Que.	1	2	3	
	Ans.	4	4	3	
BEGINNER'S BOX-5	Que.	1	2	3	4
	Ans.	3	2	4	4
BEGINNER'S BOX-6	Que.	1	2	3	4
	Ans.	1	4	1	3
BEGINNER'S BOX-7	Que.	1	2	3	4
	Ans.	3	3	4	4



EXERCISE-I (Conceptual Questions)

ATTACKING REAGENT

1. Which of the following species is an electrophile
(1) RNH_2 (2) SO_3
(3) NO_3^\ominus (4) ROH
2. Which of the following acts as a nucleophile?
(1) NO_2^\oplus (2) $:\text{CCl}_2$
(3) NH_2^\ominus (4) $\cdot\text{CH}_3$

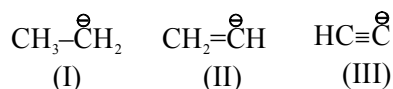
REACTION INTERMEDIATES

3. Which of the following contains only three pair of electrons :
(1) Carbanion (2) Carbocation
(3) Carbon free radical (4) None
4. Carbanion is a :-
(1) Base (2) Nucleophile
(3) Both the above (4) None

I-EFFECT

5. CH_3^\ominus is less stable than :-
(1) $\text{CH}_3-\text{CH}_2^\ominus$ (2) $\text{CH}_3-\text{CH}^\ominus-\text{CH}_3$
(3) $\text{CH}_2^\ominus-\text{NO}_2$ (4) $\text{CH}_3-\text{CH}^\ominus-\text{C}_2\text{H}_5$
6. Decreasing order of -I effect of the triad $[-\text{NO}_2, -\text{NH}_3^\oplus, -\text{CN}]$ is :-
(1) $-\text{NH}_3^\oplus > -\text{NO}_2 > -\text{CN}$
(2) $-\text{NH}_3^\oplus > -\text{CN} > \text{NO}_2$
(3) $-\text{CN} > -\text{NO}_2 > -\text{NH}_3^\oplus$
(4) $-\text{NO}_2 > -\text{CN} > -\text{NH}_3^\oplus$
7. Most stable carbanion is :-
(1) $\text{HC}\equiv\text{C}^\ominus$ (2) $\text{H}_2\text{C}=\text{C}^\ominus$
(3) $\text{CH}_3-\text{C}^\ominus(\text{CH}_3)_2$ (4) $\text{CH}_3-\text{C}^\ominus(\text{CH}_3)=\text{CH}_2$

8. The correct order of stability of given carbanions will be :-



- (1) $\text{I} > \text{II} > \text{III}$ (2) $\text{III} > \text{II} > \text{I}$
(3) $\text{I} > \text{III} > \text{II}$ (4) $\text{II} > \text{I} > \text{III}$

9. Which is most basic among the following :-

- (1) CH_3NH_2
(2) $\text{CH}_3\text{CH}_2\text{NH}_2$
(3) NH_3
(4) $(\text{CH}_3)_2\text{CHNH}_2$

10. Which of the following has maximum pK_a :-

- (1) CH_2FCOOH
(2) CH_2ClCOOH
(3) CH_3COOH
(4) HCOOH

11. Which of the following is most acidic

- (1) Methoxy acetic acid
(2) Acetic acid
(3) Chloro acetic acid
(4) Trifluoroacetic acid

12. Which of the following show + I-effect :-

- (1) $-\text{OH}$ (2) $-\text{OCH}_3$ (3) $-\text{CH}_3$ (4) $-\text{Cl}$

13. Among the following the most highly ionised in water is:

- (1) $\text{CH}_3\text{CH}_2\text{CHClCOOH}$
(2) $\text{CH}_3\text{CH}_2\text{CCl}_2\text{COOH}$
(3) $\text{CH}_3\text{CHClCH}_2\text{COOH}$
(4) $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{COOH}$

14. The strongest acid amongst the following compounds is ?

- (1) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$
(2) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$
(3) CH_3COOH
(4) HCOOH

15. Which of the following acids is stronger than acetic acid :-

- (1) Propanoic acid (2) HCOOH
(3) Butyric acid (4) $(\text{CH}_3)_2\text{CHCOOH}$

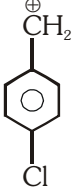
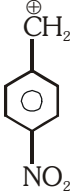
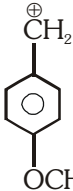
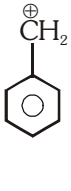


16. Which of the following acids have the lowest pK_a value :-

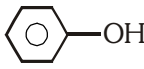
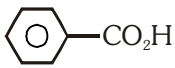
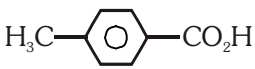
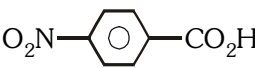
- (1) $\text{CH}_3-\overset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{COOH}$
 (2) $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{COOH}$
 (3) CCl_3COOH
 (4) CHCl_2COOH

R- OR M-EFFECT

17. Most stable carbocation is :-

- (1)  (2) 
 (3)  (4) 





18. Most acidic compound is :-

- (1) 
 (2) 
 (3) 
 (4) 

19. Which resonating structure of vinyl chloride is least stable :-

- (1) $\text{CH}_2=\text{CH}-\ddot{\text{Cl}}:$
 (2) $\overset{\ominus}{\text{C}}\text{H}_2-\text{CH}=\overset{\oplus}{\text{Cl}}$
 (3) $\overset{\ominus}{\text{C}}\text{H}_2-\overset{\oplus}{\text{C}}\text{H}-\text{Cl}$
 (4) All have equal stability

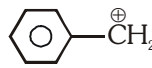
20. The stabilization due to resonance is maximum in

- (1)  (2) 
 (3)  (4) 

21. In which of the following compounds carbon-chlorine bond distance is minimum :-

- (1) CH_3-Cl
 (2) $\text{C}_6\text{H}_5-\text{CH}_2-\text{Cl}$
 (3) $\text{CH}_2=\text{CH}-\text{Cl}$
 (4) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$

22. Consider the following carbocations

- (a) $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2$ (b) 
 (c) $\text{CH}_3-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2$ (d) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$

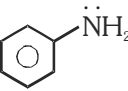
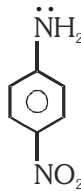
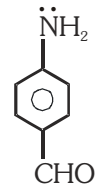
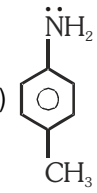
The relative stabilities of these carbocations are such that :-

- (1) $d < b < c < a$
 (2) $b < d < c < a$
 (3) $d < b < a < c$
 (4) $b < d < a < c$

23. Among the following, the strongest base is :-

- (1) $\text{C}_6\text{H}_5\text{NH}_2$
 (2) $p\text{-NO}_2-\text{C}_6\text{H}_4\text{NH}_2$
 (3) $m\text{-NO}_2-\text{C}_6\text{H}_4\text{NH}_2$
 (4) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

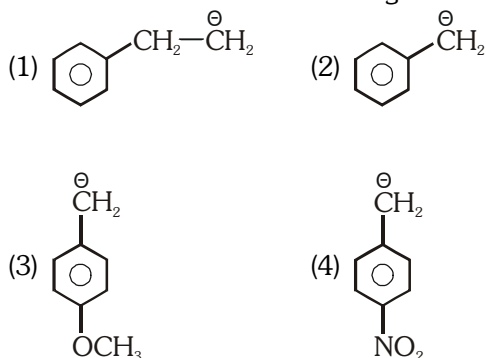
24. Arrange in decreasing order of basic strength :

- (I)  (II) 
 (III)  (IV) 

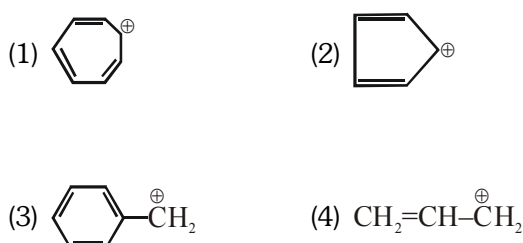
- (1) $\text{I} > \text{II} > \text{III} > \text{IV}$ (2) $\text{II} > \text{III} > \text{I} > \text{IV}$
 (3) $\text{IV} > \text{I} > \text{III} > \text{II}$ (4) $\text{IV} > \text{I} > \text{II} > \text{III}$



25. The most stable carbanion among the following is



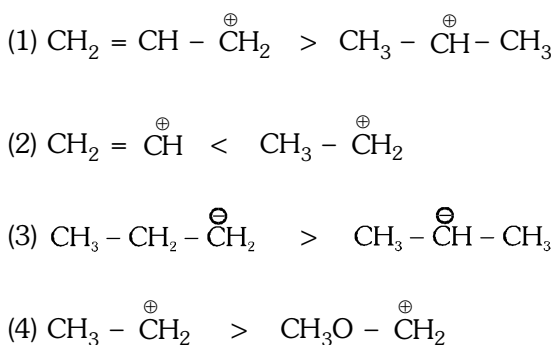
26. Which of the following is most stable carbocation:-



27. The oxygen atom in phenol –

- (1) exhibits only inductive effect
- (2) exhibits only resonance effect
- (3) has more dominating resonance effect than inductive effect
- (4) has more dominating inductive effect than resonance effect

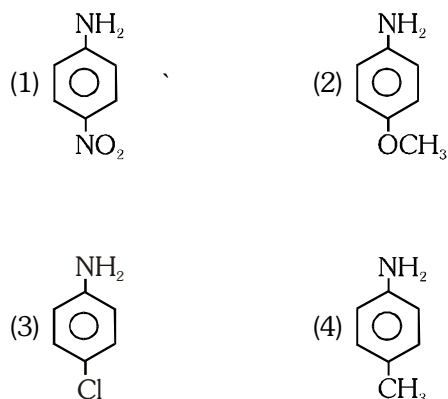
28. Which is incorrect stability order :-



29. Mesomeric effect is due to :-

- (1) Delocalization of σ e⁻
- (2) Delocalization of π e⁻
- (3) Migration of H – atom
- (4) Migration of proton

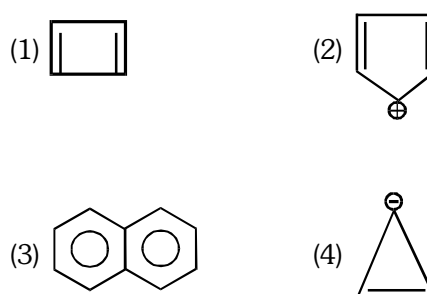
30. Which of the following is least basic :-



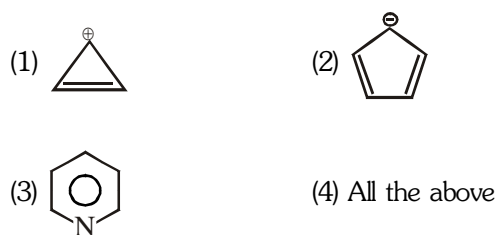
31. Among the following the pKa is minimum for :-

- (1) $\text{C}_6\text{H}_5\text{OH}$
- (2) HCOOH
- (3) $\text{C}_2\text{H}_5\text{OH}$
- (4) $\text{CH}_3\text{C}\equiv\text{CH}$

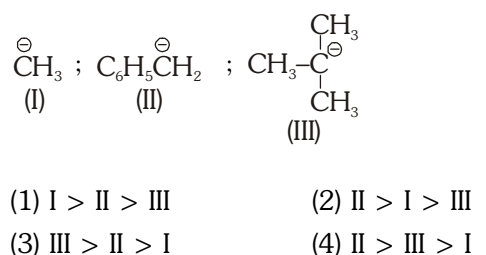
32. Among the following the aromatic compound is –



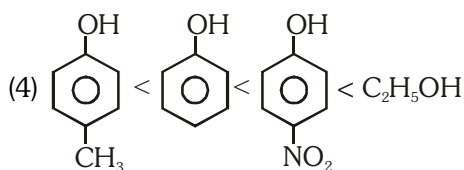
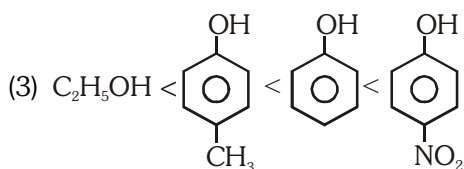
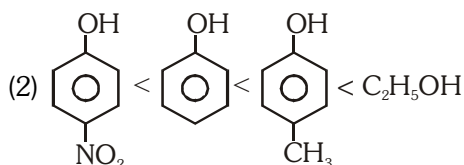
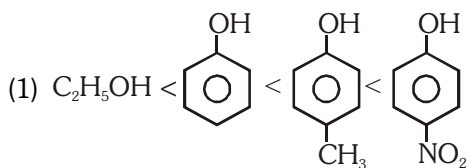
33. Which is aromatic compound among the following



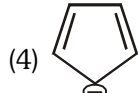
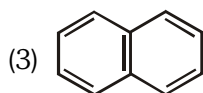
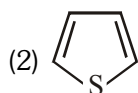
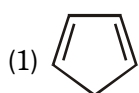
34. Select the correct option for stability of following carbanions :



35. Correct increasing order of acidity of the following phenols is :-



36. The non aromatic compound among the following is :-



37. The correct order of acidic strength of the following compounds is :-

A. Phenol

B. p-Cresol

C. m-Nitrophenol

D. p- Nitrophenol

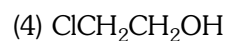
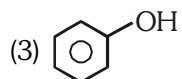
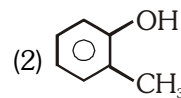
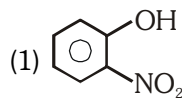
(1) $C > B > A > D$

(2) $D > C > A > B$

(3) $B > D > A > C$

(4) $A > B > D > C$

38. Which one of the following compounds is most acidic:-



39. Which of the following is most acidic :-

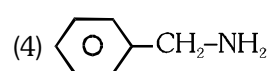
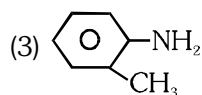
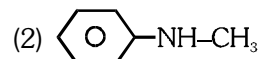
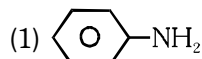
(1) phenol

(2) benzyl alcohol

(3) m-chloro phenol

(4) cyclohexanol

40. Which of the following is the strongest base :-



41. The dipole moment of vinyl chloride is lower than that of methyl chloride. This is due to :-

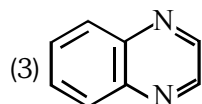
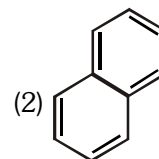
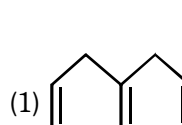
(1) Resonance effect

(2) Inductive effect

(3) Electromeric effect

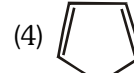
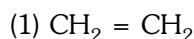
(4) Hyperconjugation

42. Which is Aromatic compound :-



(4) 2 and 3 both

43. Which of the following is the most acidic compound :-



44. Among the following the strongest acid is :-

- (1) CH_3COOH
- (2) $\text{C}_6\text{H}_5\text{COOH}$
- (3) $m\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$
- (4) $p\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$



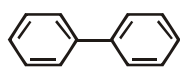

45. The least reactive chlorine is present in -

- (1) Methyl chloride
- (2) Allyl chloride
- (3) Ethyl chloride
- (4) Vinyl chloride

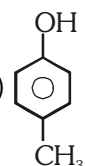
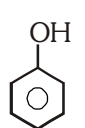
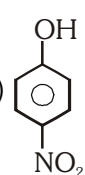
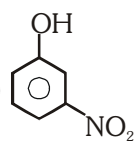
46. Which one of the following resonating structures of 1-methoxy-1,3-butadiene is least stable :-

- (1) $\overset{\ominus}{\text{C}}\text{H}_2\text{-CH=CH-CH}=\overset{\oplus}{\text{O}}\text{-CH}_3$
- (2) $\text{CH}_2=\text{CH}-\overset{\ominus}{\text{C}}\text{H-CH}=\overset{\oplus}{\text{O}}\text{-CH}_3$
- (3) $\overset{\ominus}{\text{C}}\text{H}_2-\overset{\oplus}{\text{C}}\text{H-CH=CH-O-CH}_3$
- (4) $\text{CH}_2=\text{CH-CH=CH-O-CH}_3$

47. Four structures are given in options (a) to (d). Examine them and select the aromatic structures.

- (a)  (b) 
- (c)  (d) 
- (1) a and d (2) b and c
(3) a and b (4) a and c

48. Order of acidic strength of the following compound will be :

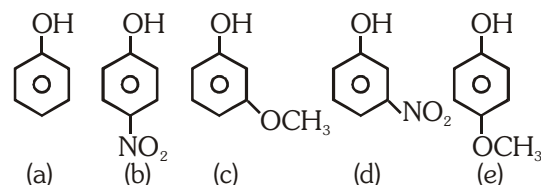
- (A)  (B) 
- (C)  (D) 

- (1) $\text{C} > \text{D} > \text{B} > \text{A}$ (2) $\text{D} > \text{C} > \text{B} > \text{A}$
(3) $\text{A} > \text{B} > \text{C} > \text{D}$ (4) $\text{B} > \text{A} > \text{C} > \text{D}$

49. Phenol is less acidic than

- (1) Ethanol
- (2) o-Nitrophenol
- (3) o-Methylphenol
- (4) o-Methoxyphenol

50. Mark the correct order of decreasing acid strength of the following compounds.



- (1) $e > d > b > a > c$ (2) $b > d > a > c > e$
(3) $e > d > c > b > a$ (4) $b > d > c > a > e$

HYPERCONJUGATION

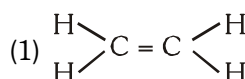
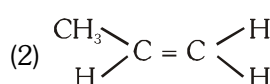
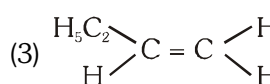
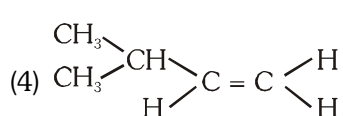
51. Which of the following compounds exhibits hyperconjugation :

- (1) Phenol
- (2) Ethyne
- (3) Ethanol
- (4) Propene

52. Which of the following is least stable :-

- (1) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$
- (2) $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{C}}\text{H}_2$
- (3) $\text{CH}_3-\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}_3$
- (4) $\text{CH}_3-\overset{\oplus}{\text{C}}(\text{CH}_3)_2-\text{CH}-\text{C}_6\text{H}_5$

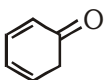
53. Which of the following is most stable alkene :-

- (1) 
- (2) 
- (3) 
- (4) 

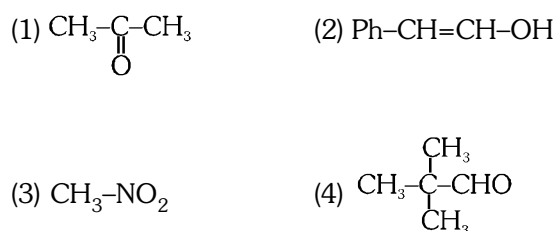


54. The correct order of increasing stability of the given alkenes is
- (1) 1-pentene > cis-2-pentene > trans-2-pentene > 2-methyl-2-butene
 - (2) 1-pentene > trans-2-pentene > cis-2-pentene > 2-methyl-2-butene
 - (3) 1-pentene < cis-2-pentene < trans-2-pentene < 2-methyl-2-butene
 - (4) 1-pentene < trans-2-pentene < cis-2-pentene < 2-methyl-2-butene

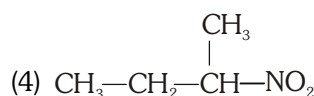
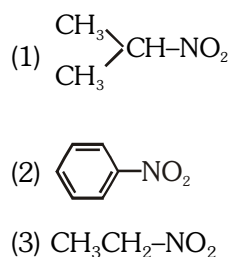
TAUTOMERISM

55. Tautomerism is due to :-
- (1) Delocalization of sigma electrons
 - (2) Delocalization of pi electrons
 - (3) Migration of active-H-atom
 - (4) None is correct
56. Which of the following will lead to maximum enolisation :-
- (1) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
 - (2) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$
 - (3) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{Br}}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
 - (4) 
57. Urea $\left[\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \right]$ molecule exhibits (isomerism):-
- (1) Chain
 - (2) Position
 - (3) Geometrical
 - (4) Tautomerism

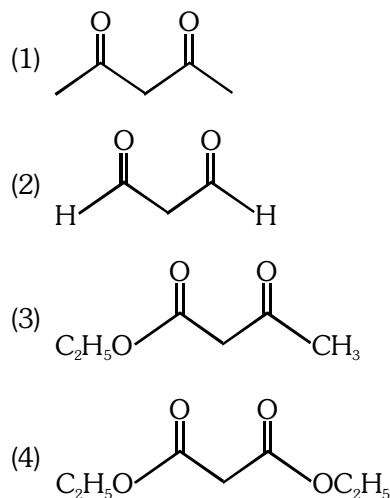
58. Tautomerism is not observed in :-



59. Which of the following is not soluble in NaOH solution :



60. Which of the following has highest enol content.



EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	3	2	3	3	1	1	2	4	3	4	3	2	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	3	4	3	4	3	1	4	3	4	1	3	4	2	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	3	4	2	3	1	2	1	3	4	1	4	4	3	4
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	4	1	2	4	4	2	2	3	3	4	4	4	2	2



Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** Tertiary carbonium ions are generally formed more easily than primary carbonium ions.
Reason :- Hyperconjugative as well as inductive effect of additional alkyl groups stabilize tertiary carbonium ions.
 (1) A (2) B (3) C (4) D
- Assertion :-** Carbanions have ammonia like pyramidal shape.
Reason :- The carbon atom carrying negative charge has an octet of electrons.
 (1) A (2) B (3) C (4) D
- Assertion :-** Pyrrole is a weaker base than its hydrogenated product pyrrolidine.
Reason :- Lone pair of electrons on nitrogen is delocalized in pyrrole.
 (1) A (2) B (3) C (4) D
- Assertion :-** A mixture of o-nitrophenol and p-nitrophenol can be separated by steam distillation.
Reason :- o-nitrophenol is steam volatile but p-nitrophenol is not.
 (1) A (2) B (3) C (4) D
- Assertion :-** The carbocation $\text{CF}_3 - \text{CH}_2^+$ is less stable than CF_3^+ .
Reason :- In case of $\text{CF}_3 - \text{CH}_2^+$, the strongly electron withdrawing $-\text{CF}_3$ group intensifies the +ve charge but in case of CF_3^+ , the lone pairs of electrons on each of the three F-atoms overlap with the empty p-orbital of the carbocation carbon atom, thereby dispersing the +ve charge.
 (1) A (2) B (3) C (4) D
- Assertion :-** Acidity of the following compounds decreases in the order $\text{HC}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}_3$
Reason :- Acidity of the compounds increase as the electronegativity of the carbon increases to which H is attached.
 (1) A (2) B (3) C (4) D
- Assertion :-** The acidity of alcohols follows the order : $1^\circ > 2^\circ > 3^\circ$.
Reason :- The + I effect of the additional alkyl groups favours the cleavage of O-H bond.
 (1) A (2) B (3) C (4) D
- Assertion :-** Phenol is less acidic than p-nitro phenol.
Reason :- Phenolate ion is more stable than p-nitro phenolate ion.
 (1) A (2) B (3) C (4) D
- Assertion :-** Pyrrole is more basic than pyridine.
Reason :- In pyrrole, nitrogen is sp^3 -hybridized.
 (1) A (2) B (3) C (4) D
- Assertion :-** Aniline is a weaker base than benzyl amine.
Reason :- In aniline, mesomeric interaction occurs between benzene ring and amino group.
 (1) A (2) B (3) C (4) D
- Assertion :** Cyclopentadienyl anion is much more stable than allyl anion.
Reason : Cyclopentadienyl anion is aromatic in character.
 (1) A (2) B (3) C (4) D
- Assertion :** Acetic acid is stronger acid than ethyl alcohol.
Reason : In acetate ion both C-O bond lengths are equal.
 (1) A (2) B (3) C (4) D



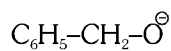
13. **Assertion :** Tropylium ion is more stable than benzyl cation.

Reason : Tropylium ion is anti-aromatic in nature.

(1) A (2) B (3) C (4) D

14. **Assertion :-** Phenol is more acidic than benzyl alcohol.

Reason :- $C_6H_5-O^{\ominus}$ is more stable than



(1) A (2) B (3) C (4) D

15. **Assertion :-** Picric acid is stronger acid than phenol.

Reason :- Picric acid has $-COOH$ group, while phenol has $-OH$ group.

(1) A (2) B (3) C (4) D

16. **Assertion :-** Pyridine is less basic than trimethyl amine.

Reason :- Nitrogen atom in pyridine is sp^2 hybridized, while in trimethylamine it is sp^3 .

(1) A (2) B (3) C (4) D

17. **Assertion :-** Enol form of cyclohexane-1,3,5-trione is more stable than its keto form.

Reason :- It contains α -hydrogen atoms.

(1) A (2) B (3) C (4) D

18. **Assertion :-** $C_2H_5NO_2$ shows functional isomerism as well as tautomerism.

Reason :- Nitroethane shows tautomerism due to presence of α -hydrogens and functional isomerism with ethyl nitrite.

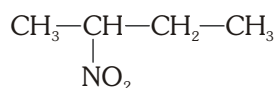
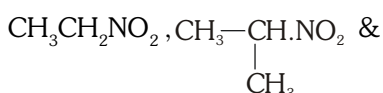
(1) A (2) B (3) C (4) D

19. **Assertion :** Tautomers have different functional group.

Reason : Tautomers have same molecular formula.

(1) A (2) B (3) C (4) D

20. **Assertion :-** The following compound are given below –



all three compounds are soluble in NaOH.

Reason :- All above compound have lower boiling than CH_3NO_2 .

(1) A (2) B (3) C (4) D

21. **Assertion :-** Phenol is stronger acid than alcohols.

Reason :- Phenol is stabilized by resonance whereas alcohols are not.

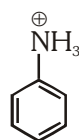
(1) A (2) B (3) C (4) D

22. **Assertion :-** Formic acid is a stronger acid than benzoic acid.

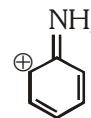
Reason :- pK_a of formic acid is higher than that of benzoic acid.

(1) A (2) B (3) C (4) D

23. **Assertion :-** Here two structures are given



I



II

I and II are not acceptable canonical structure.

Reason :- Carbonium ions are less stable than ammonium ions.

(1) A (2) B (3) C (4) D

24. **Assertion :-** Benzene hexachloride is an aromatic compound.

Reason :- It contain 3π bonds in the ring.

(1) A (2) B (3) C (4) D

25. **Assertion :-** $Cl-\underset{\substack{| \\ C_2H_5}}{CH}-CH_3$ and $H-\underset{\substack{| \\ CH_3}}{CH}-Cl$ are

enantiomers.

Reason :- Non-superimposable mirror images are known as enantiomers.

(1) A (2) B (3) C (4) D

26. **Assertion :-** Dimethyl amine has more basic strength than trimethyl amine.

Reason :- It is due to solvation effect.

(1) A (2) B (3) C (4) D

27. **Assertion :-** In $\begin{matrix} CH_3 \\ | \\ C=CH_2 \\ | \\ CH_3 \end{matrix}$, the C-C-C bond

angles are different.

Reason :- The C has steric effect of $-CH_3$ group.

(1) A (2) B (3) C (4) D



28. Assertion :- Benzyl amine is more basic than ethyl amine.

Reason :- Phenyl group has +I effect.

(1) A (2) B (3) C (4) D

29. Assertion :- o-nitrophenol is more acidic than m-nitrophenol.

Reason :- At o-position, -I effect of $-\text{NO}_2$ is more than at m-position.

(1) A (2) B (3) C (4) D

30. Assertion :- N, N-diethylethane is more basic than N, N-dimethyl methane.

Reason :- +I of ethyl is more than methyl group.

(1) A (2) B (3) C (4) D

31. Assertion :- Dimethyl amine has more basic strength than trimethyl amine.

Reason :- It is due to solvation effect.

(1) A (2) B (3) C (4) D

32. Assertion :- In $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$, the C-C-C bond

angles are different.

Reason :- The C has steric effect of $-\text{CH}_3$ group.

(1) A (2) B (3) C (4) D

33. Assertion :- Benzyl amine is more basic than ethyl amine.

Reason :- Phenyl group has +I effect.

(1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	2	1	1	1	1	3	3	4	1	1	2	3	1	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	2	1	2	3	2	3	2	4	1	1	1	4	2	1
Que.	31	32	33												
Ans.	1	1	4												

